February 5, 1880.

THE PRESIDENT in the Chair.

The Presents received were laid on the table and thanks ordered for them.

The following Papers were read :—

I. "On the Spectra of the Compounds of Carbon with Hydrogen and Nitrogen." By G. D. LIVEING, M.A., F.R.S., Professor of Chemistry, and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge. Received February 2, 1880.

In a memoir "On the Spectra of Metalloids" ("Nova Acta Reg. Soc. Upsal.," ser. iii, vol. ix), Ångström and Thalèn have made a careful analysis of the different spectra assigned to carbon. They distinguish four sets of groups of shaded bands produced under different circumstances, which they define, besides the line spectrum which they ascribe to carbon itself. Of these four sets of bands, two sets, situated at the extremities of the spectrum, they show to be produced in the combustion of cyanogen, a third to be common to all the hydrocarbons, and the fourth to be produced by carbonic oxide. The first two sets, the third, and the fourth sets respectively, they observed to be produced also in the electric discharge between carbon electrodes according as it took place in nitrogen, hydrogen, or oxygen. Their observations on this subject appear to us almost conclusive. Nevertheless, other observers have, since their publication, maintained different opinions.

The spectrum of hydrocarbons burning in air has been repeatedly described: first by Swan in 1856, and afterwards by Attfield, Watts, Morren, Plücker, Boisbaudran and others, and has been given in detail by Piazzi Smyth ("End on Illumination in Private Spectroscopy"). The characteristic part of this spectrum consists of four groups of bands of fine lines in the orange, yellow, green, and blue respectively, and we refer hereafter to these as the hydrocarbon bands. These four groups, according to Plücker and Hittorf, also constitute the spectrum of the discharge of an induction coil in an atmosphere of hydrogen between carbon electrodes. They are also conspicuous in the electric discharge in olefiant gas at the atmospheric and at reduced pressures.

The descriptions of the other less conspicuous parts of the spectrum

of the flame of hydrocarbons are not all concordant. Boisbaudran notices, besides the four hydrocarbon bands, only two hazy bands in the indigo. Watts ("Phil. Mag.," 1869 and 1871) and Piazzi Smyth give the same two bands somewhat wider, and resolved into a series of fine lines. These two observers are in substantial agreement about this part of the spectrum, but Piazzi Smyth notices in addition a faint haze in the red below C.

Plücker and Hittorf notice the entire absence in the flame of olefiant gas of the two bright groups of lines (blue and violet as described below) characteristic of the flame of cyanogen, and the presence of a series of dark lines on a violet background in a position intermediate between those of the two cyanogen groups. A similar description is given by Morren ("Ann. Ch. et Phys.," Mars, 1865). Neither of these observers notices the two hazy bands above-mentioned. The descriptions given by these authors of this series of dark lines appear to relate to something not seen by the other observers. They resemble in some respects the description of the corresponding part of the spectrum of the electric discharge in vapour of sulphur, and we think it highly probable that these lines were due to some compound of sulphur derived from the sulphuric acid employed in preparing the gas.

Several observers also have described the spectrum of the flame of burning cyanogen. Faraday, as long ago as 1829, called the attention of Herschel and Fox Talbot to it, and the latter, writing of his observations ("Phil. Mag.," ser. iii, vol. iv, p. 114), points out as a peculiarity that the violet end of the spectrum is divided into three portions with broad dark intervals, and that one of the bright portions is ultra-violet. More recently Dibbits, Morren, Plücker and Hittorf, have particularly described this spectrum. Dibbits ("Pogg. Ann.," 1864) mentions in the cyanogen flame fed with oxygen, a series of orange and red bands shaded on the less refrangible side (*i.e.*, in the opposite way to the hydrocarbon bands), the four hydrocarbon bands more or less developed, a group of seven blue lines, a group of two or three faint blue (indigo) lines, then a group of six violet lines, and, lastly, a group of four ultra-violet lines. When the cyanogen is burnt in air the hydrocarbon bands are less developed, and the three faint indigo lines are scarcely visible, but the rest of the spectrum is the same, only less brilliant.

Plücker and Hittorf ("Phil. Trans.," 1865) state that in the flame of cyanogen burning in air under favourable circumstances, the orange and yellow groups of lines characteristic of burning hydrocarbons are not seen, the brightest line of the green group appears faintly, the blue group is scarcely indicated; but a group of seven fluted bands in the blue, three in the indigo, and seven more in the violet, are well developed, especially the last. When the flame was fed with oxygen

instead of air, they state that an ultra-violet group of three fluted bands appeared. They notice also certain red bands with shading in the reverse direction, which are better seen when the flame is fed with air than with oxygen. Other observers give similar accounts, noticing the brilliance of the two series of bands in the blue and violet above mentioned, and that they are seen equally in the electric discharge through cyanogen. All do not notice the ultra-violet group, but this is no doubt owing to the absorption of these rays by the prisms employed, for photographs which we have taken of the spectrum of the cyanogen flame in air show this group strongly developed.

These three bright groups of bands of fine lines are as characteristic of the flame of cyanogen and of the spark in that gas, as the four hydrocarbon bands are of the flame of hydrocarbons.

The flame of carbonic oxide shows nothing but a continuous spectrum. The series of bands seen in the spark in an oxide of carbon are well known, and there is not, so far as we know, any dispute about them. The brightest of them appears to have been seen by some observers in the flame produced by the combustion of other compounds of carbon.

The contention of Ångström and Thalèn is that the channelled spectra of the hydrocarbon and cyanogen flames are the spectra of acetylene and cyanogen, and not of carbon itself, and that in the flame of burning cyanogen we sometimes see the spectrum of the hydrocarbon superposed on that of the cyanogen, the latter being the brighter; and that in vacuum tubes containing hydrocarbons the cyanogen spectrum observed is due to traces of nitrogen.

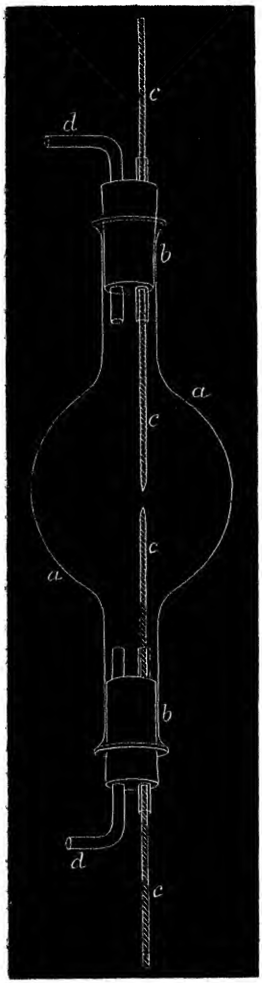
No chemist who remembers the extreme sensibility of the spectroscopic test, and the difficulty, reaching almost to impossibility, of removing from apparatus and material the last traces of air and moisture, will feel any surprise at the presence of small quantities of either hydrogen or nitrogen in any of the gases experimented on.

Mr. Lockyer ("Proc. Roy. Soc.," vol. xxvii, p. 308) has recently obtained a photograph of the arc in chlorine, which shows the series of fluted bands in the ultra-violet, on the strength of which he throws over the conclusion of Ångström and Thalèn, and draws inferences as to the existence of carbon vapour above the chromosphere in the coronal atmosphere of the sun, which, if true, would be contrary to all we know of the properties of carbon. We cannot help thinking that these bands were due to the presence of a small quantity of nitrogen.

Our faith in the conclusions of Ångström and Thalèn on this subject has been much strengthened by our own observations, which we now proceed to describe.

The following experiments were made with a De Meritens dynamo-electric machine, arranged for high tension, giving an alternating

current capable of producing an arc between carbon poles in air of about 10 millims. in length. The carbon poles used were 3 millims. in diameter, and had been previously purified by prolonged heating in a current of chlorine. This treatment, though it removes



a large part of the metallic impurities present in the commercial carbons, will not remove the whole, so that lines of calcium, iron, magnesium, and sodium may still be recognised in the arc. Besides the traces of metallic impurities a notable quantity of hydrogen always remains unremovable by treatment with chlorine; and we are

not at present aware of any practicable method by which it can be got rid of.

The arc was taken in different gases inside a small glass globe (*aa* in figure) about 60 millims. in diameter, blown in the middle of a tube. The two ends of the tube (*bb*) were closed with dry corks, through which were passed (1) the carbons (*cc*), inserted through two pieces of narrow glass tubing, and a packing of platinum foil; (2), two other glass tubes (*dd*) through which currents of the gases experimented with were passed.

Spectrum of the Arc in Air.

The arc taken in a globe of air gave a tolerably bright continuous spectrum, superposed on which the green and blue hydrocarbon bands were seen, also the seven bands in the blue (wave-lengths 4600 to 4502, Watts) as in the flame of cyanogen, three faint bands, or lines, in the indigo (wave-lengths about 4364·5, 4371·5, 4381·5), and much more brightly the six bands in the violet (wave-lengths 4220 to 4158, Watts) and five ultra-violet (wave-lengths about 3883·5, 3871, 3862, 3854·5, 3850.) Besides these bands, lines of iron, calcium, and sodium were visible. The arc in this case was practically taken in a mixture of nitrogen and carbonic oxide, for in a short time the oxygen of the air is converted into carbonic oxide, as was shown by the flame which always filled the globe on stopping the arc for a second or two.

Spectrum of the Arc in Carbonic Acid Gas.

On passing through the globe continuously a current of carbonic acid gas, the seven bands in the blue, and those in the violet and ultra-violet gradually died out until they ceased to be at all visible continuously, and when now and then momentarily seen were only just discernible. On the other hand, the hydrocarbon bands, yellow, green, and blue, came out stronger and were even brilliant. Lines of iron and calcium were still visible. On stopping the current of carbonic acid gas and allowing air to diffuse into the globe, the violet and ultra-violet bands soon began to appear and presently became permanent and bright, the hydrocarbon bands remaining bright.

Spectrum of the Arc in Hydrogen.

The globe had next a continuous current of dry hydrogen passed through it. The arc, contrary to what would be expected from the behaviour of the spark discharge in hydrogen, would not pass through more than a very short space, very much less than in air or carbonic acid gas. There was a tolerably bright continuous spectrum, no trace of the seven bands in the blue, or of those in the violet or ultra-violet, and no metallic lines, but a fairly bright line in the red, which we identi-

fied, by comparison with the spark in a vacuum tube, with the C line of hydrogen. The F line, identified in like manner, was also seen as a faint diffuse band. This last line was in general overpowered by the continuous spectrum, but was regularly seen, when, from some variation in the discharge, the continuous spectrum became less brilliant. This was the first occasion on which we had seen the hydrogen lines in the arc at all, though Secchi ("Compt. Rend.," 1873) states that he had seen them by the use of moist carbon poles. We tried to repeat his experiment, without success. The hydrocarbon bands in the green and blue were at intervals well seen. Those in the yellow and orange were, owing doubtless to the smaller dispersion of the light in that region, overpowered by the continuous spectrum. Whereas when air and carbonic acid gas were used, the inside of the globe was quickly covered with dust from the disintegrated poles, scarcely any, if any, such dust was thrown off when the arc was passed in hydrogen.

Spectrum of the Arc in Nitrogen.

Nitrogen was next substituted for the hydrogen. A longer arc would now pass, the seven blue, the violet and ultra-violet bands all came out well, at intervals brilliantly. The green and blue hydrocarbon bands were also well developed.

Spectrum of the Arc in Chlorine.

On filling the globe with chlorine and keeping a current of that gas passing through it, the arc would not pass through a greater distance than about 2 millims. No metallic lines were visible. At first the violet bands, as well as the green and blue hydrocarbon bands, were visible, but gradually when the current of chlorine had been passing for some minutes, there was nothing to be seen but a continuous spectrum with the green and blue hydrocarbon bands. Neither of these bands were strong, and at intervals the blue bands disappeared altogether.

Spectrum of the Arc in Carbonic Oxide.

When the globe, previously full of air, was filled with carbonic oxide and a current of that gas passed through it, the arc would not pass through any greater space than in chlorine. There was much continuous spectrum; the yellow, green, and blue hydrocarbon bands were well seen, some of the seven blue bands were just discernible, the violet had nearly, and the ultra-violet quite, gone from sight. No trace of the carbonic oxide bands, as seen in the spark discharge in that gas, was visible. This is the more remarkable since under similar circumstances two of the characteristic lines of hydrogen were seen.

Spectrum of the Arc in Nitric Oxide.

In this gas a very long arc could be obtained. The violet and ultra-violet bands were well seen, the seven blue bands were seen but weaker. The blue and green hydrocarbon bands were also seen well when the arc was short, not so well when the arc was long. The length of the arc did not seem to affect the brightness of the violet bands. Many metallic lines of iron, calcium, and magnesium were seen.

Spectrum of the Arc in Ammonia.

In ammonia only a short arc could be obtained. All the bands were faint, but the seven blue, the violet and ultra-violet bands were always visible.

These experiments with different gases eliminate to a large extent the influence of electric conductivity on the character of the spectrum; but we intend to examine more thoroughly the effect of this variable by observation of the arc in some of these gases under different conditions of pressure.

Spectra of Flames of Carbon Compounds.

Besides the experiments with the arc above described, we have made some observations of the spectra of flames of sundry compounds of carbon.

In the flame of cyanogen, prepared from well dried mercury cyanide, passed over phosphoric anhydride inserted in the same tube, and burnt from a platinum jet fused into the end of the tube, we found, as Plücker and Hittorf had found, that the hydrocarbon bands were almost entirely absent, only the brightest green band was seen, and that faintly. The seven blue and the violet bands on the other hand were, as described by other observers, well developed, the three indigo bands less brightly. A series of bands at the red end, also described by Dibbits and by Plücker and Hittorf, was also visible. These bands are sharply defined on the more refrangible side and fade away on the other side, and extend beyond the orange hydrocarbon bands on the red side. They have not been seen by us in the spectra of the arc, but they may very well have been present in some of those spectra and yet not seen because of the continuous spectrum of the arc, which, not being very much dispersed at the red end, was bright enough to overpower any such bands. This continuous spectrum seems much stronger when well purified carbon electrodes are used than when they contain metallic impurities to the extent commonly present in them. We may remark that in general we see only six bands, or rather six maxima of light, in the violet series, as stated by Dibbits, not seven, as stated by Morren and by Plücker and Hittorf; and in the ultra-violet we always see five maxima of light, instead of four as given by

Dibbits, and three given by Plücker and Hittorf. These ultra-violet bands are well developed in the flame of cyanogen burning in air and are readily photographed, and easily seen when quartz lenses and calcite prisms are employed.

The flame of hydrocyanic acid burning in air showed very much the same as that of cyanogen.

In the flame of a mixture of hydrogen and carbon disulphide, made by passing purified hydrogen through a tube containing carbon disulphide so as to be nearly or quite saturated with the vapour, and burning it in air, no hydrocarbon bands at all could be detected.

Nor could any hydrocarbon bands be detected in the flame of a mixture of carbonic oxide and hydrogen burnt in air.

When a mixture of hydrogen with carbon tetrachloride vapour was burnt, hydrocarbon bands made their appearance, but were rather weak.

The flame of carbonic oxide mixed with vapour of carbon tetrachloride showed faint traces of hydrocarbon bands occasionally, but not continuously.

On the other hand, chloroform, carefully prepared from chloral and fractionated, when mixed with hydrogen, gave, when burnt in air, the hydrocarbon bands very strongly. When it was mixed with carbonic oxide instead of hydrogen it still gave the hydrocarbon bands, but not nearly so strongly as with hydrogen.

On a review of the whole series of observations, certain points stand out plainly. In the first place, the seven blue, the violet, and ultra-violet bands, characteristic of the flame of cyanogen, are conspicuous in the arc taken in an atmosphere of nitrogen, air, nitric oxide, or ammonia, and they disappear, almost, if not quite, when the arc is taken in a non-nitrogenous atmosphere of hydrogen, carbonic oxide, carbonic acid, or chlorine. These same bands are seen brightly in the flames of cyanogen and hydrocyanic acid, but are not seen in those of hydrocarbons, carbonic oxide, or carbon disulphide. The conclusion seems irresistible that they belong to cyanogen; and this conclusion does not seem to us at all invalidated by the fact that they are seen weakly, or by flashes, in the arc or spark taken in gases supposed free from nitrogen, by reason of the extreme difficulty of removing the last traces of air. They are never, in such a case, the principal or prominent part of the spectrum, and in a continuous experiment they are seen to fade out in proportion as the nitrogen is removed. This conclusion is strengthened by the observations of one of us, that cyanogen (or hydrocyanic acid) is generated in the arc in atmospheric air in large quantity. Also in the experiment above described with the arc in nitrogen, we have found that when the current of nitrogen issuing from the globe is passed through a solution of potash the solution soon gives the reactions of a cyanide.

In the next place, the green and blue bands, characteristic of the hydrocarbon flame, are well seen when the arc is taken in hydrogen; but though less strong when the arc is taken in nitrogen or in chlorine, they seem to be always present in the arc, whatever the atmosphere. This is what we should expect, if they be due, as Ångström and Thalèn suppose, to acetylene; for we have found that the carbon electrodes always contain, even when they have been long heated in chlorine, a notable quantity of hydrogen.

In the flames of carbon compounds they by no means always appear; indeed, it is only in those of hydrocarbons or their derivatives that they are well seen. Carbonic oxide and carbon disulphide, even when mixed with hydrogen, do not show them; and if seen in the flames of cyanogen, hydrocyanic acid, and carbon tetrachloride mixed with hydrogen, they are faint, and do not form a principal or prominent part of the spectrum. This is all consistent with the supposition of Ångström and Thalèn. The fact that the bands are not produced even in the presence of hydrogen, when it is not present in the flame in the form of a compound with carbon, is very significant; for we know that acetylene is present, and can easily be extracted from the flame of any hydrocarbon, and that it is formed as a proximate product of decomposition of hydrocarbons by the electric discharge, but we have no evidence that it is producible as a product of direct combination of carbon with hydrogen at the comparatively low temperature of a flame such as we have mentioned.

The hydrocarbon bands are best developed in the blowpipe flame, that is under conditions which appear, at first sight, unfavourable to the existence of acetylene in the flame. We have, however, satisfied ourselves, by the use of a Deville's tube, that acetylene may readily be withdrawn from the interior of such a flame, and from that part of it which shows the hydrocarbon bands most brightly.

The question as to whether these bands are due to carbon itself or to a compound of carbon with hydrogen, has been somewhat simplified by the observations of Watts and others on the spectrum of carbonic oxide. There is, we suppose, no doubt now that that compound has its own spectrum quite distinct from the hydrocarbon flame spectrum. The mere presence of the latter spectrum feebly developed in the electric discharge in compounds of carbon supposed to contain no hydrogen, appears to us to weigh very little against the series of observations which connect this spectrum directly with hydrocarbons.

In the next place, it appears conclusively from the experiments, that the development of the violet bands of cyanogen, or the less refrangible hydrocarbon bands, is not a matter of temperature only. For the appearance of the hydrogen lines C and F in the arc taken in hydrogen, indicates a temperature far higher than that of any flame. Yet the violet bands are not seen in hydrogen at that temperature, while

the green bands are well developed. The violet bands are, nevertheless, seen equally well at the different temperatures of the flame, arc, and spark, provided cyanogen be the compound under observation in the flame, and nitrogen and carbon are present together at the higher temperatures of the arc and spark.

The similarity in the character of the magnesium-hydrogen spectrum, which we have described, to the green band of the hydrocarbons is very striking. We have similar bright maxima of light, succeeded by long drawn out series of fine lines, decreasing in intensity towards the more refrangible side. This peculiarity, common to both, impels the belief that it is a consequence of a similarity of constitution in the two cases, and that magnesium forms with hydrogen a compound analogous to acetylene. In this connexion the very simple relation (2 : 1) between the atomic weights of magnesium and carbon is worthy of note, as well as the power which magnesium has, in common with carbon, of combining directly with nitrogen. We may with some reason expect to find a magnesium-nitrogen spectrum.

Apart from the mere relative electric conductivity of gases, it is clear, from the foregoing experiments, that the length and the character of a discontinuous electric discharge in different gases does not follow the law which we should expect. It will require a prolonged series of experiments to arrive at definite conclusions on this matter, but it appears to us, in the mean time, highly probable that one of the main factors in producing these remarkable variations in the arc will be found to be the relative facility with which the carbon electrode combines with a gaseous medium.

The interest attaching to the question of the constitution of comets, especially since the discovery by Huggins ("Proc. Roy. Soc.," xvi, p. 386; xxiii, p. 154; "Phil. Trans.," 1868, p. 555), that the spectra of various comets are all identical with the hydrocarbon spectrum, naturally leads to some speculation in connexion with the conclusions to which our experiments point. Provided we admit that the materials of the comet contain ready formed hydrocarbons and that oxidation may take place, then the acetylene spectrum might be produced at comparatively low temperatures without any trace of the cyanogen spectrum, or of metallic lines. Such reactions might be brought about by the tidal disturbances involving collisions and projections of the constituents of the swarms of small masses circulating in orbits round the sun, which we have every reason to believe constitute the cometic structure. If, on the other hand, we assume only the presence of uncombined carbon and hydrogen, we know that the acetylene spectrum can only be produced at a very high temperature; and if nitrogen were also present, that we should have the cyanogen spectrum as well. Either then the first supposition

is the true one, not disproving the presence of nitrogen; or else the atmosphere which the comet meets is hydrogen and contains no free nitrogen.

II. "On the Epipubis in the Dog and Fox." By T. H. HUXLEY, Sec. R.S. Received January 30, 1880.

In 1871* I gave a brief description of a structure which I had observed in the dog, in the following terms:—

"In the myology of the dog, the insertion of the tendon of the external oblique muscle of the abdomen presents some interesting peculiarities. The outer and posterior fibres of this muscle end in a fascia, which is partly continued over the thigh as *fascia lata*, and partly forms an arch (Poupart's ligament) over the femoral vessels; by its inner end it is inserted into the outer side of a triangular fibro-cartilage, the broad base of which is attached to the anterior margin of the pubis, between its spine and the symphysis, while its apex lies in the abdominal parietes. The internal tendon of the external oblique unites with the tendon of the internal oblique to form the inner pillar of the abdominal ring, and is inserted into the inner side of the triangular fibro-cartilage. The *pectineus* is attached to the ventral face of the cartilage; the outer part of the tendon of the rectus into its dorsal face; but the chief part of that tendon is inserted into the pubis behind it. This fibro-cartilage appears to represent the marsupial bone, or cartilage, of the Monotremes and Marsupials."

The only reference to this statement which I have met with is by Professor Macalister, in his "Introduction to the Systematic Zoology and the Morphology of Vertebrate Animals" (1878), p. 265:—

"Professor Huxley describes a fibro-cartilaginous 'marsupial' above the pubis, from whose anterior surface the pectineus arises. I have failed to satisfy myself of its existence as a constant structure in many dogs, in the common and Bengal foxes, in the dingo, jackal, *Canis pallipes*, and wolf."

The wording of this passage does not make it quite clear whether the writer has not found the structure in any case, but does not mean to deny that it may occur occasionally in the various *Canidæ* he mentions; or whether he has found it occasionally, but not constantly, in all or some of them.

Under these circumstances, it may be desirable to publish the fact that, having recently dissected, for purposes of comparison, a male and female fox and a male and female dog, I have not had the slightest difficulty in demonstrating the existence of the structure which I described

* "Manual of the Anatomy of Vertebrated Animals," p. 417.